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SUBSTITUTION OF BIPHENYLOXIDE FOR CHLORIDE ON
HEXAPHENYLDICHLOROTETRAPHOSPHONITRILE

by

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THESIS

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The Kinetics and Mechanism for the Substitution of Biphenyloxide

for Chloride on Hexaphenyldichlorotetraphosphonitrile

by

John Hay McCorry
Lieutenant Commander, United States Navy
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Submitted in partial fulfillment of the
requirements for the degree of

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ABSTRACT

In this research a study of the kinetics and mechanism of the biphenyloxide substitution for chloride on the hexaphenyldichlorotetra-phosphonitrile molecule was conducted. The reaction was studied in sealed, evacuated ampuoles at 210°C and in an evacuated gas pressure measuring system at temperatures of 185°C and 195°C.

Two isomers of the expected disubstituted product were isolated by fractional recrystalization from acetonitrile. The isomers had melting points of 204°C and 174°C.

The gas pressure studies provided extent of reaction versus time curves. An analog computer was used to simulate the reaction and the rates obtained were used to determine the <u>Entropy of activation</u> as -42.5 ± 10.0 cal mole^{-1} degree K^{-1} and <u>Enthalpy of activation</u> as 13.6 ± 10.0 Kcal mole^{-1} for the first substitution.

A mechanism consistent with these values is proposed and discussed.

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FIGURE

I. INTRODUCTION

For the past fifteen years, numerous studies have been under-
taken to improve the quality of phosphonitrile organic-inorganic
polymers. The work described in this report was undertaken with the
hope of determining the reaction mechanism for the polymerization of
hexaphenyldichlorotetraphosphonitrile and bisphenol. It seemed likely
that this could offer the key for improving such polymers.

Since the bisphenol caused ring linkage of varying degree thereby
making isolation and characterization of a product virtually impossible,
this study was conducted using p-hydroxybiphenyl as the nucleophile.
This would prevent polymerization from occurring and thus allow
isolation and characterization of the product. This nucleophile was
chosen because it closely resembles bisphenol sterically as well as
in acidity.

Isolation of this reaction product, the twice substituted tetramer,
was reported in (1).

In 1834, LIEBIG announced the discovery of trimeric

chlorophosphonitrile (2).   Little was done with this discovery until

the latter part of the nineteenth century, when an American chemist

H. N. STOKES prepared an isolated series of chlorophosphonitrile

polymers $(NPCl_2)_n$, where n = 3-7 (3, 4, 5, 6, 7, 8, 9).   The important

structural characteristic of this series is the unsaturated repeating

unit (I).

$$-\!\!\left(\begin{matrix} X\ X \\ \backslash\,/ \\ P \end{matrix} = N\right)_{\!\!m}$$
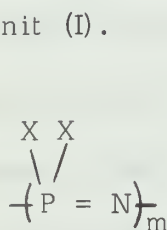
(I)
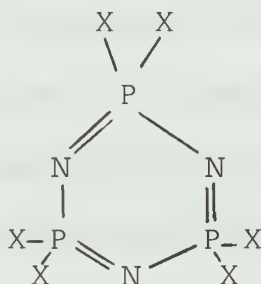
(II)
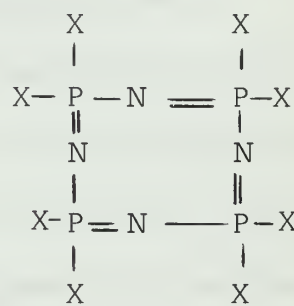
(III)

STOKES (9) proposed a planar cyclic structure for hexachloro-

triphosphonitrile (II).   This structure was confirmed by electron

diffraction measurements of (II) by BROCKWAY and BRIGHT (10) and

SCHOMAKER (11).   Structural determination from x-ray diffraction

patterns by KETLAAR and deVRIES (12, 13) showed octachlorotetra-

phosphonitrile (III) to be a puckered, eight-membered ring containing

alternate nitrogen and phosphorous atoms, with two chlorine atoms

attached to each phosphorous.

Again, little was done in the study of phosphonitriles until the nineteen fifties when a great need developed for a flame resistant polymer for high temperature use. Many hoped to find the answer to this problem in a phosphonitrile inorganic polymer. The available reviews of these efforts include PADDOCK (14), SHAW et al (15), SCHMULBACH (16) and HABER (17). Although all are excellent, HABER's work is particularly germane to this article, because it was his associates at the NAVAL ORDNANCE LABORATORY, CORONA, CALIF., who carried out most of the work leading to the problem reported here.

The group at CORONA developed numerous synthetic procedures for placing different inorganic and organic substituents where desired on a wide variety of cyclic and linear phosphonitriles. Of specific interest was HERRING and DOUGLAS' (18) syntheses of hexaphenyldichlorotetra-phosphonitrile compound (IV) in reasonable yields by the reaction:

$$\phi_2 PCl + \phi PCl_2 + NaN_3 \implies$$

$$
\begin{array}{ccccc}
 & \phi & & \phi & \\
 & | & & | & \\
Cl - & P & - N = & P & -- \phi \\
 & \| & & | & \\
 & N & & N & \\
 & | & & \| & \\
\phi - & P & = N - & P & - Cl \\
 & | & & | & \\
 & \phi & & \phi & \\
\end{array}
$$

(IV)
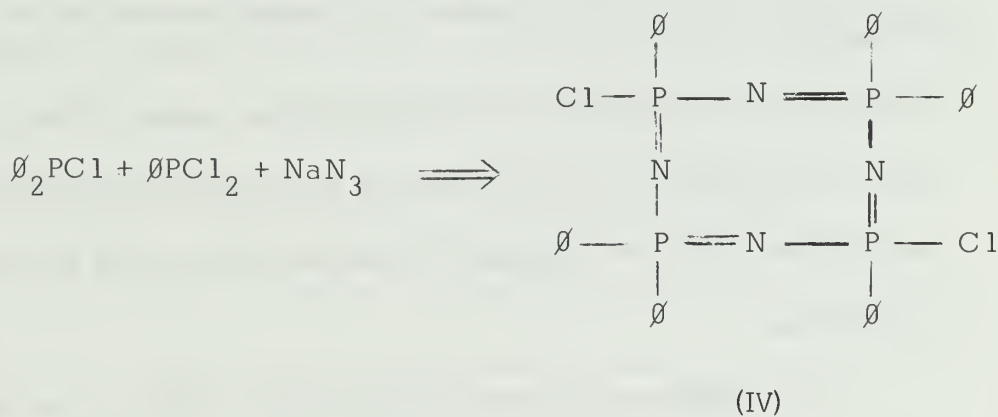
This compound has been shown to exist in both _trans_ (mp 303–304 °C) and _cis_ (mp 189–190 °C) configurations.

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The work at CORONA finally evolved into a search for a satisfactory ring linkage of the above mentioned dichlorotetraphosphonitrile, to form organic-inorganic polymers.

The notation hereafter used in discussing the dichlorohexaphenyl-tetraphosphonitrile will be that adopted by the CORONA group (18), namely the hexaphenyltetraphosphonitrile structure (V) is hereafter abbreviated as ☐ or ◇ and in the case of cyclic monomers as $\underline{T}$ only.

$$
\begin{array}{ccccc}
\varnothing & & \varnothing & & \\
| & & | & & \\
-P & - N = & P & - \varnothing \\
\parallel & & | & & \\
N & & N & & \\
| & & \parallel & & \\
\varnothing - P & = N - & P & - \\
| & & | & & \\
\varnothing & & \varnothing & &
\end{array}
$$
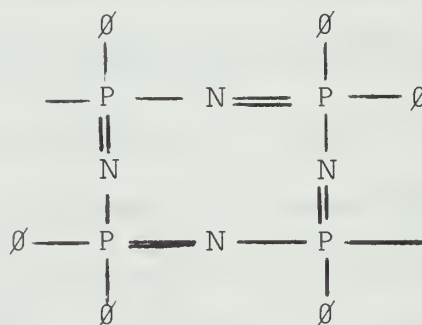
(V)

Among the studies reported in (1), were the thermal isomerization of the trans TCl_2 to $\underline{cis}$ TCl_2 at 265°C and chemical isomerization by refluxing thionylchloride with the hydrolysis product $T(OH)_2$ in chloroform. Of interest is the fact that use of phosphorouspentachloride as the chlorinating agent produces no isomerization under the same conditions.

Diaminohexaphenyltetraphosphonitrile, $T(NH_2)_2$, was prepared by bubbling ammonia gas into a chloroform suspension of TCl_2. Polymerization attempts on $T(NH_2)_2$ produced the expected structure $(◇-NH-)_x$.

(However x could not be forced above 2.)   In other diamine studies

it was found that HCl cleaved dimethylamino groups from the T ring with

nearly quantitative regeneration of TCl_2.

Additional polymerization attempts were made using diols.   The

most common experimental technique was the use of the diol in the melt

as solvent.   The reactions were always run at temperatures above 210°C,

under vacuum and with continuous withdrawal of any gases evolved.

Most of the reactions were run with either resorcinol or bisphenol as

the ring linking agent.

Polymers which had fractions with molecular weights as high as

269,000 were obtained.   The softening range of these polymers was

180-220°C.   In general, they were hard, glossy, brittle, amber solids

at room temperature.

In the bisphenol-TCl_2 studies, all attempts to increase the

quality of the polymer product by varying the reaction conditions failed.

III. EXPERIMENTAL

A. PURIFICATION OF STARTING MATERIALS

1. Twice Recrystalized Tetramer

Three gms of once recrystalized TCl_2 per hundred ml of chlorobenzene were refluxed for twelve hours. The solution was allowed to cool to room temperature by slowly lowering the heating mantle over a period of two hours. After twelve hours, the crystalized TCl_2 was dried under vacuum (mp 299-301°C).

2. Once Recrystalized Tetramer

Approximately three gms of commercial TCl_2 per hundred ml of chlorobenzene were set to boiling until all TCl_2 dissolved in chlorobenzene. The solution was then allowed to cool for twenty-four hours. TCl_2 crystalized out as a coating on the beaker. The chlorobenzene was decanted and the TCl_2 scraped into a weighing bottle and set to drying under vacuum (mp 292-295°C).

3. p-Hydroxybiphenyl

A solution of 50% water and 50% EtOH was set to boiling and p-hydroxybiphenyl was added until it would no longer go into solution. At this point, more solvent mixture was added until all the p-hydroxybiphenyl was in solution. After standing for twenty-four hours, the solvent was decanted and the wet p-hydroxybiphenyl was set to drying under vacuum (mp 163.5-164.5°C).

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B.   SEALED AMPUOLE TESTS

In an approximate ratio of four moles of p-hydroxybiphenyl to one mole of TCl_2, the starting materials were weighed separately into a five-inch test tube.   The material was carefully placed in the test tube to insure that none of the material was adhering to the upper portion of it. The test tubes were then sealed under vacuum.   No measurement of the actual pressure was made on any of these test tubes.   It is estimated, however, that the pressure varied from twenty mm to two hundred mm of Hg.

For a given test, all the sealed tubes were simultaneously immersed into an electrically controlled oil bath at 210°C.   At varying time intervals, the tubes were removed from the oil bath and washed with benzene to remove the oil.

The test tubes were then placed in four hundred ml beakers and covered with three hundred ml of distilled water.   The tubes were then broken, allowing the water into the tube to absorb any HCl produced by the reaction.   Using a pH meter, the resulting solution was then titrated with NaOH solution which had been standardized against KHP.

After the water had evaporated from the above beakers, the material remaining in the broken test tubes was washed with boiling benzene into 25 ml erlenmeyer flasks.   The benzene was evaporated off.   The remaining solid was washed with cold acetonitrile and allowed to stand. After approximately twelve hours, the liquid portion was decanted into another flask.   The solid remaining in the original flask was put into

solution with a minimum of boiling acetonitrile. After approximately

twelve hours, the liquid was once again decanted into a third flask and

the crystals which were left behind were dried under vacuum. These

crystals were weighed and mp determinations made. All of this material

was later recrystalized to obtain a sample which had an mp of 201-203°C;

(ir 3145, 3072, 3056, 3033, 3012, 2995, 2922, 2851, 1958, 1891, 1601,

1512, 1481, 1449, 1436, 1311, 1290, 1202, 1164d, 1114d, 1067, 1036,

1024, 1017, 1008, 996, 891d, 841, 792, 763, 745, 718, 705, 691, 660d,

638, 612, 573, 553, 531, 521, 511, 450 cm^{-1}).

Analysis (for $T(0\emptyset\emptyset)_2$)

	P	N	C	H	Cl
Calc'd	12.68	5.72	73.5	4.9	0.0
Found	12.4	5.8	73.3	4.9	0.08

The second solution from which the above product was obtained, was

allowed to sit for approximately one week, after which, in a number of

cases, additional crystals were found to have formed. These crystals

were dried under vacuum and weighed. These crystals were found to

have a melting point of 172-173°C; (ir 3074, 3057, 3029, 3009, 2991,

1953, 1887, 1601, 1509, 1480, 1448, 1433, 1311, 1290, 1201, 1192,

1171, 1161, 1114, 1063, 1035, 1023, 1015, 1006, 994, 887d, 839,

793, 772, 758, 741, 713, 705, 687, 659, 632, 615, 572, 554, 542,

533, 509, 451 cm^{-1}).

Analysis (for $T(0\emptyset\emptyset)_2$)

	P	N	C	H	Cl
Calc'd	12.68	5.72	73.5	4.9	0.0
Found	12.5	5.9	73.6	5.0	0.11

The two materials described above will be referred to as high melter (mp 204 °C) and low melter (mp 174 °C) $T(O\emptyset\emptyset)_2$.

C. SEALED SYSTEM WITH HCl ABSORBER

Reaction vessels were manufactured which would allow for KOH to be used as an HCl absorber without being in the reaction melt. A simple line diagram of the apparatus is shown in Figure 1.

For these tests, the p-hydroxybiphenyl and the TCl_2 were separately weighed into one of the tapered joint test tubes. Approximately 0.5 gms of KOH were then added to the second tapered joint test tube. The tubes were then smeared with silicone grease and the joints secured with wire to prevent losing the test tubes in the oil bath in the event of a failure.

The rig was then placed under vacuum (approximately 2 mm Hg) and the KOH heated to drive off any possible water. After sealing and removing from the vacuum system, the rig was immersed into the oil bath at various temperatures for various lengths of time.

At the end of the desired time, the rig was removed from the oil bath and plunged into an ice bath to quench the reaction. After the material in the rig solidified, the adherent oil was removed with benzene and the rig opened to the air. The test tube containing the KOH was removed and weighed to determine if there had been a significant change in weight. In all cases, there was less than 0.1 gms change in weight.

The test tube containing the reaction material was then washed with the boiling benzene and transferred to a fifty ml erlenmeyer flask.

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Ball and Socket
Joint

Vacuum Stopcock

Tapered Joint

Wire Preventers

Reaction Melt
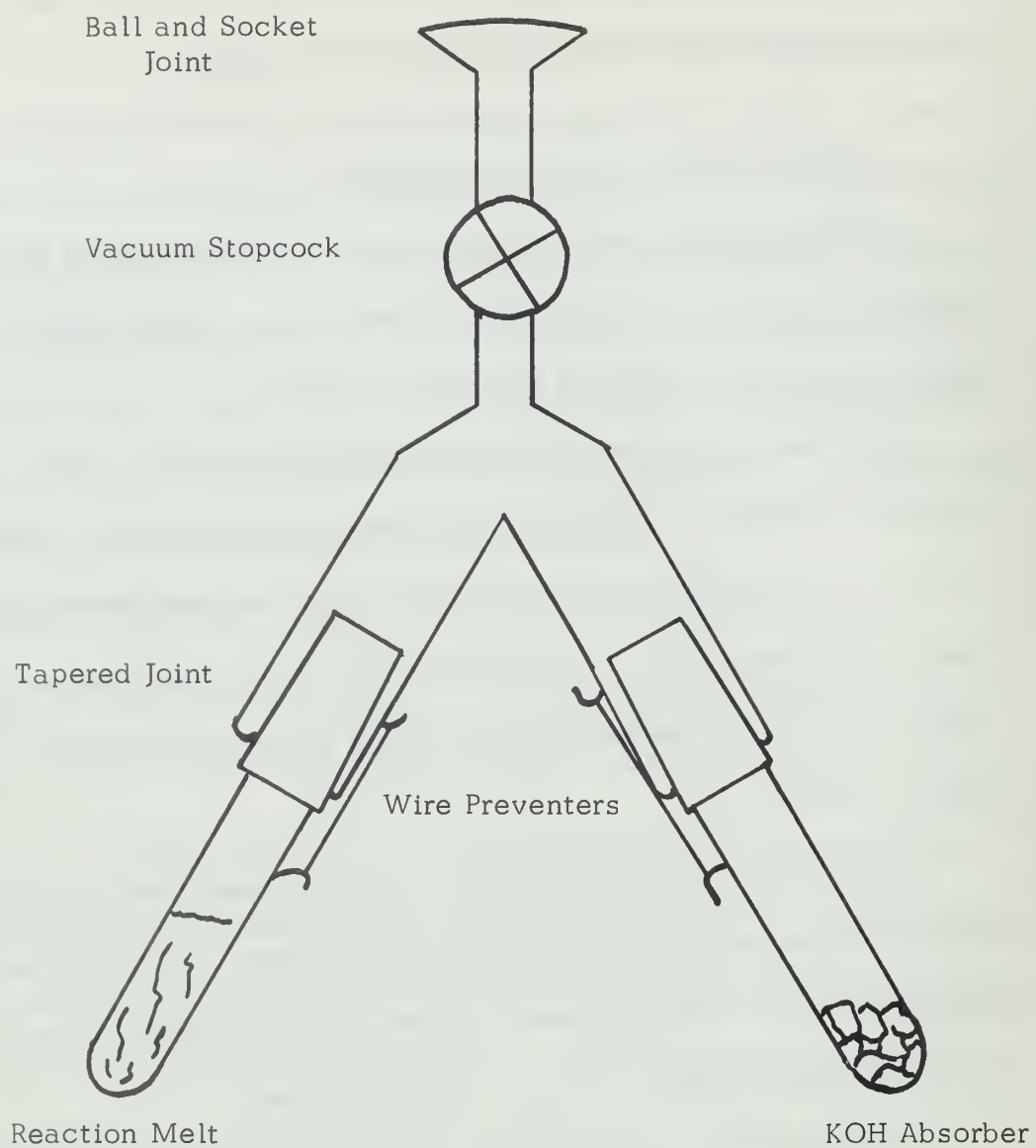
KOH Absorber

Reaction Vessel for 210°C KOH Absorber Runs

Figure 1

In all cases, there was a varying amount of material which did not go into solution in the boiling benzene; this material had an mp of 275-285°C and is considered to be contaminated TCl_2. The benzene was then evaporated from the fifty ml flask and then dried under vacuum. The flasks were weighed. In general, the flasks were found to contain between 85-95 percent of the mass of the original materials. This material was washed with cold acetonitrile and allowed to stand for approximately six hours. The cold acetonitrile solution was decanted to another flask and the remaining insoluble material was put into solution with a minimum amount of boiling acetonitrile.

The boiling solution was set aside for twenty-four hours to allow for recrystalization, after which the liquid was decanted to another flask. After allowing this second flask to evaporate to the atmosphere for about twenty-four hours, additional crystals were formed. These crystals, as well as those first recrystalized, were dried in vacuum and found to be mostly high melting $T(0\emptyset\emptyset)_2$. However, in some cases a small quantity of the low melter could be detected in the second recrystalization.

The liquid which was decanted from the first acetonitrile cold wash was found to recrystalize some material on standing to the air, which could be purified to both high and low melting $T(0\emptyset\emptyset)_2$. In addition, the remaining material could be separated by sublimation at 130°C into pure p-hydroxybiphenyl and a sticky brownish material, mp 52-58°C; (ir 3074, 3058, 3032, 2926, 2855, 1602, 1512, 1482, 1435, 1310,

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1285, 1204, 1200, 1175, 1163, 1115d, 1093, 1035, 1023, 1015,

1005, 994, 900, 841, 800, 775, 761, 744, 713, 691, 642, 612, 572,

552, 530, 510, 450 cm^{-1}).

Analysis (for T(0$\emptyset\emptyset$)$_2$)

	P	N	C	H	Cl
Calc'd.	12.68	5.72	73.5	4.9	0.0
Found	11.25	5.02	73.34	4.99	0.29

D.   DTA STUDIES

1.   Isomerization of TC1$_2$

A sample of once recrystalized TC1$_2$ was heated in the DTA

to its melting point and cooled.   When run a second time, there were

two melting points noted, one at 61°C and one at 285°C.   Upon a second

cooling and reheating, the amount of material melting at the lower mp

was found to be greater than on the previous run.   As would be expected,

there was less high melter also.   On the next cycle, it was found that

all the material melted at 60°C.

2.   p-Hydroxybiphenyl TC1$_2$ Reaction Studies

An arbitrary amount of once recrystalized TC1$_2$ mixed with

p-hydroxybiphenyl in a one-to-four molar ratio was placed in the DTA.

The DTA was then heated at 20°C per minute to 210°C.   At 165°C, the

$\emptyset\emptyset$0H was found to begin melting.   At about 175°C, it was apparent that

some exothermic reaction was taking place and that some material was

leaving the sample.   This differed markedly from a pure $\emptyset\emptyset$0H run, in

which the material melted 165°C, but there was no sign of significant

sublimation until at least 245°C.

E.   GAS PRESSURE STUDIES

These studies were undertaken utilizing an existing vacuum system and mounted manometer.   A reaction vessel was constructed which could be attached to the existing system by a ball and socket joint.   The reaction vessel's base was specifically made large enough to accommodate a half-inch stirrer.

For a specific run, approximately 2 gms of each of the starting materials were carefully weighed into the reaction vessel.   The reaction vessel was then installed on the vacuum system and evacuated to 10 microns pressure.   After the reaction vessel was satisfactorily evacuated, an oil bath mounted on an electric stirrer was raised quickly to engulf the reaction chamber.   This oil bath was controlled by manual adjustments to a variac.   The temperature was controlled to $\pm 0.5°C$.   The changes in the pressure of the system were recorded versus time.   At the beginning of the reaction, readings were taken every fifteen seconds, as the reaction passed the ten-minute mark, the intervals between readings were changed to thirty seconds.   At the twenty-minute point, the interval for readings was lengthened to one minute.   Readings were continued until the system reached equilibrium.

Such runs were made twice at 185°C and three times at 195°C. On two of the runs after equilibrium was reached, the temperature was raised in steps to 195°C, 205°C and 210°C.   At each of these temperatures, a new equilibrium was established.   The temperature was then lowered in steps to 205°C, 195°C, 185°C and 175°C.   At each temperature, equilibrium was established again.

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When the reaction vessel was removed from the vacuum system, it was found that some of the p-hydroxybiphenyl had sublimed to a point in the neck of the reaction vessel just above what had been the level of hot oil. The amount of material which had sublimed was not determined. It was noted that the sublimed material occupied a volume equal to three quarters of a cubic centimeter. The sublimation appeared to be complete within ten minutes of the start of reaction. No attempt was made to include this loss of p-hydroxybiphenyl in the later calculations. It has been assumed that the error would be relatively constant between runs.

In addition, after one of the runs, the gas in the system was collected and analyzed in a mass spectrometer. This analysis showed a relatively high percentage of water equal to one-third the total gas. This high percentage is attributed to the fact that all the moisture which was present in the collecting container was not completely removed before collecting the gas. Assuming this to be true, it was found that 95% of the gas was HCl. The remaining peaks could generally be attributed to the solvents which had earlier been used to purify the starting materials.

The data for the first fifteen minutes of each gas run were plotted and are shown as Figures 2 through 6.   In addition, the data was graphed to determined whether the reaction was first or second order. These graphs indicated that the reaction was second order.

Based on this and the assumption that the reaction goes through an intermediate of the form $ClTO\emptyset\emptyset$, an attempt was made to fit the output of an analog computer to the graphs of pressure versus time, Figures 2 through 6.   The analog computer was programmed to solve the three differential equations

$$\frac{d(C)}{dt} = k_1 (A)(B) + k_2 (D)(B) - k_{-1} (C)(D) - k_{-2} (C)(P)$$

$$\frac{d(D)}{dt} = k_1 (A)(B) + k_{-2}(C)(P) - k_{-1}(C)(D) - k_2 (D)(B)$$

$$\frac{d(P)}{dt} = k_2 (D)(B) - k_{-2} (C)(P)$$

corresponding to a reaction formulated as

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D$$

$$D + B \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C + P$$

where, $A = TCl_2$

   $B = HO\emptyset\emptyset$

   $C = HCl$

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Figure 2

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Run 195 B

H0∅∅ = 0.6400 moles liter^{-1}
TCl$_2$ = 0.1550 moles liter^{-1}
Melt volume = 20 ml

Figure 3

25

Figure 4

26

Run 185 A

$H0\emptyset\emptyset = 0.6100$ moles liter^{-1}
$TCl_2 = 0.1220$ moles liter^{-1}
Melt volume = 14.0 ml

Figure 5

Figure 6

28
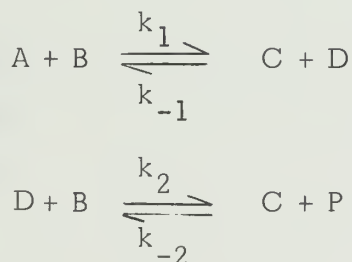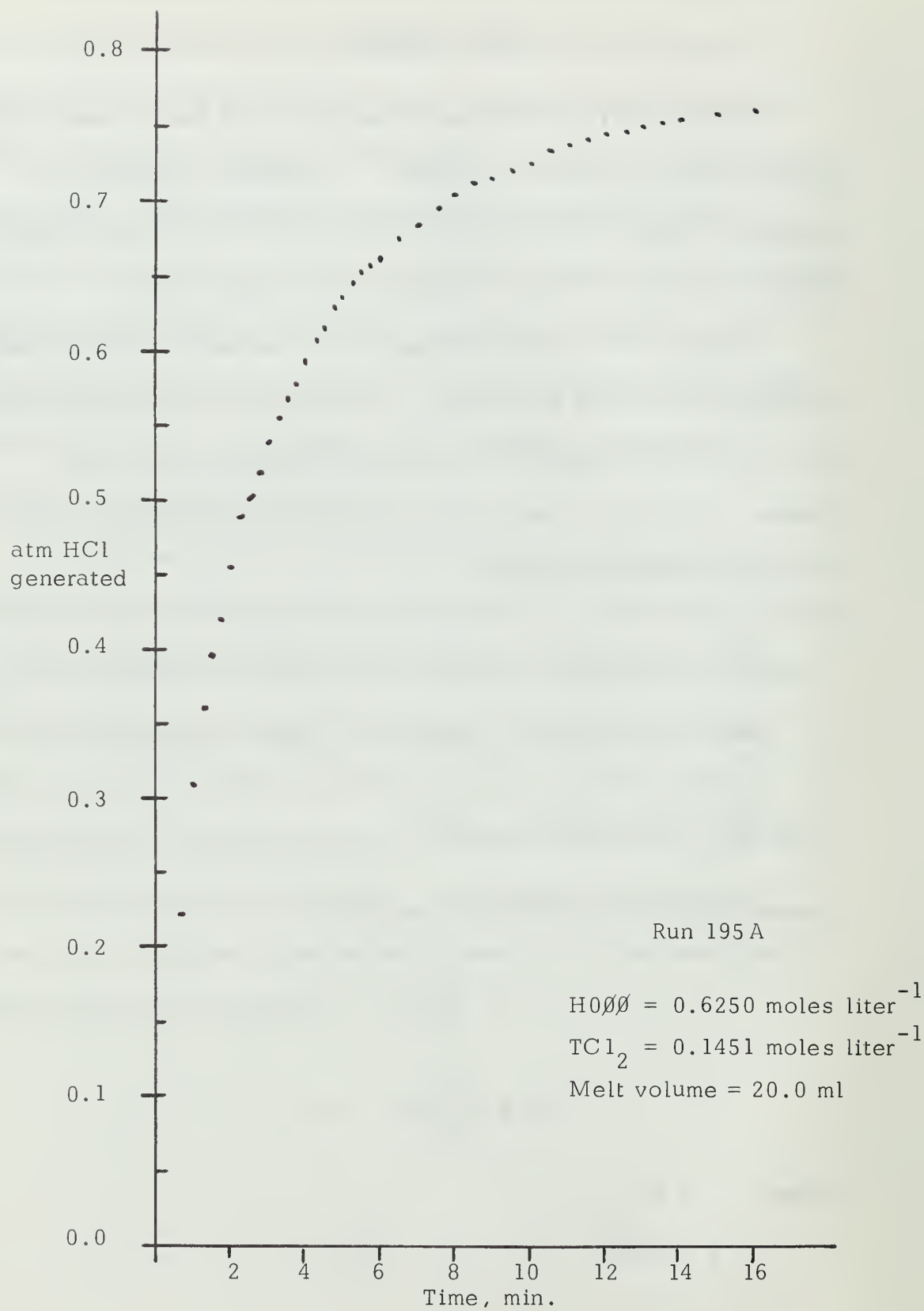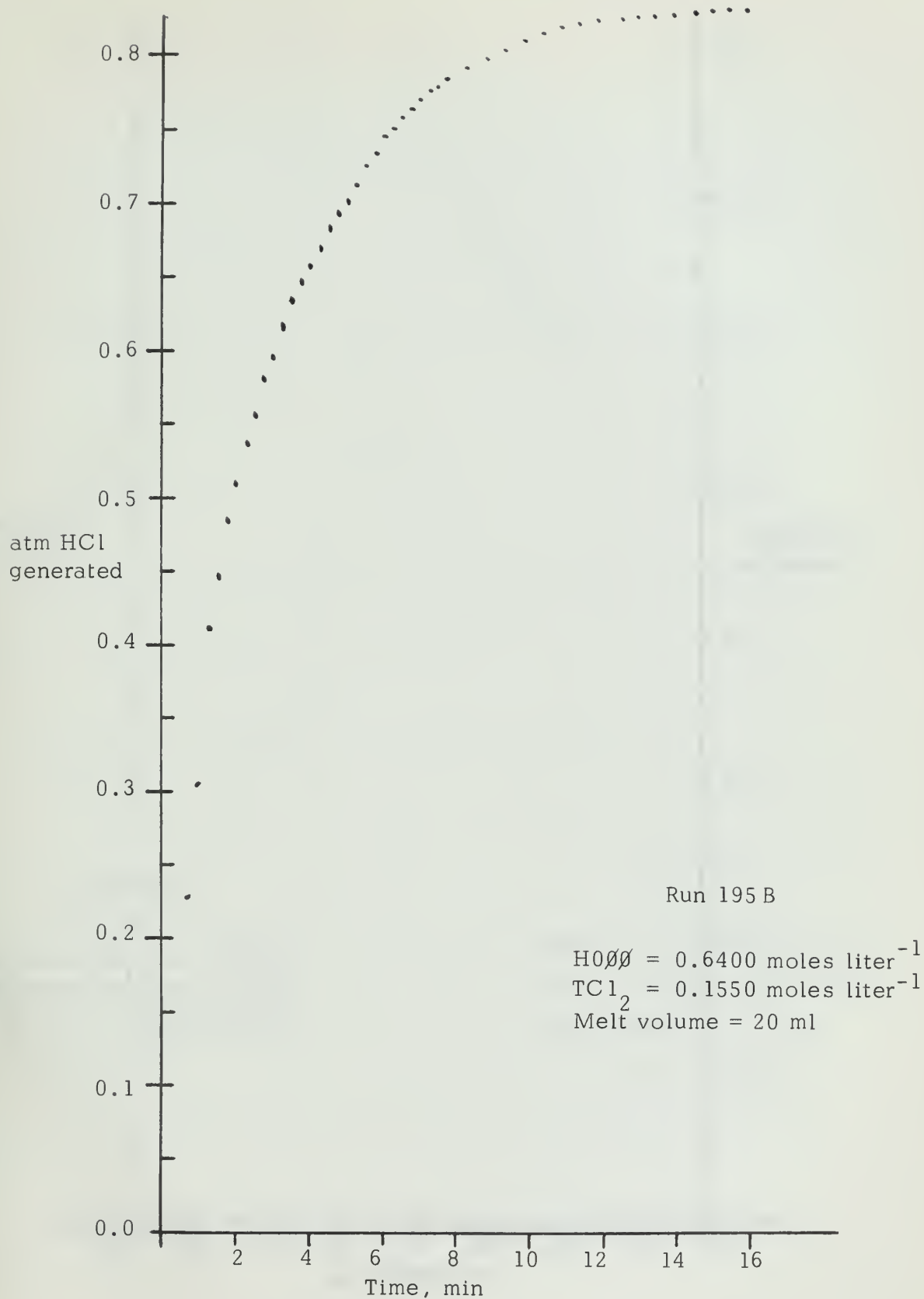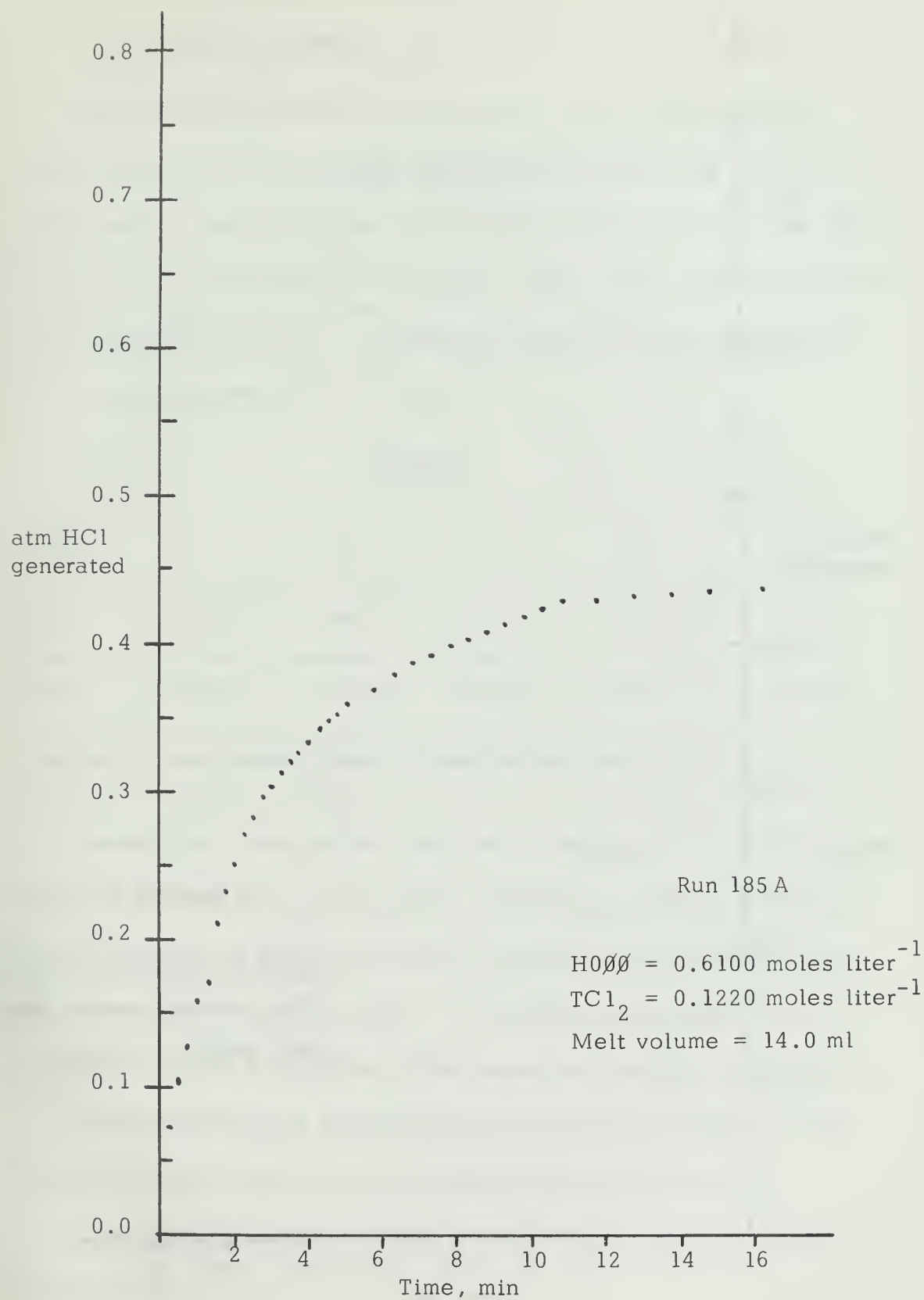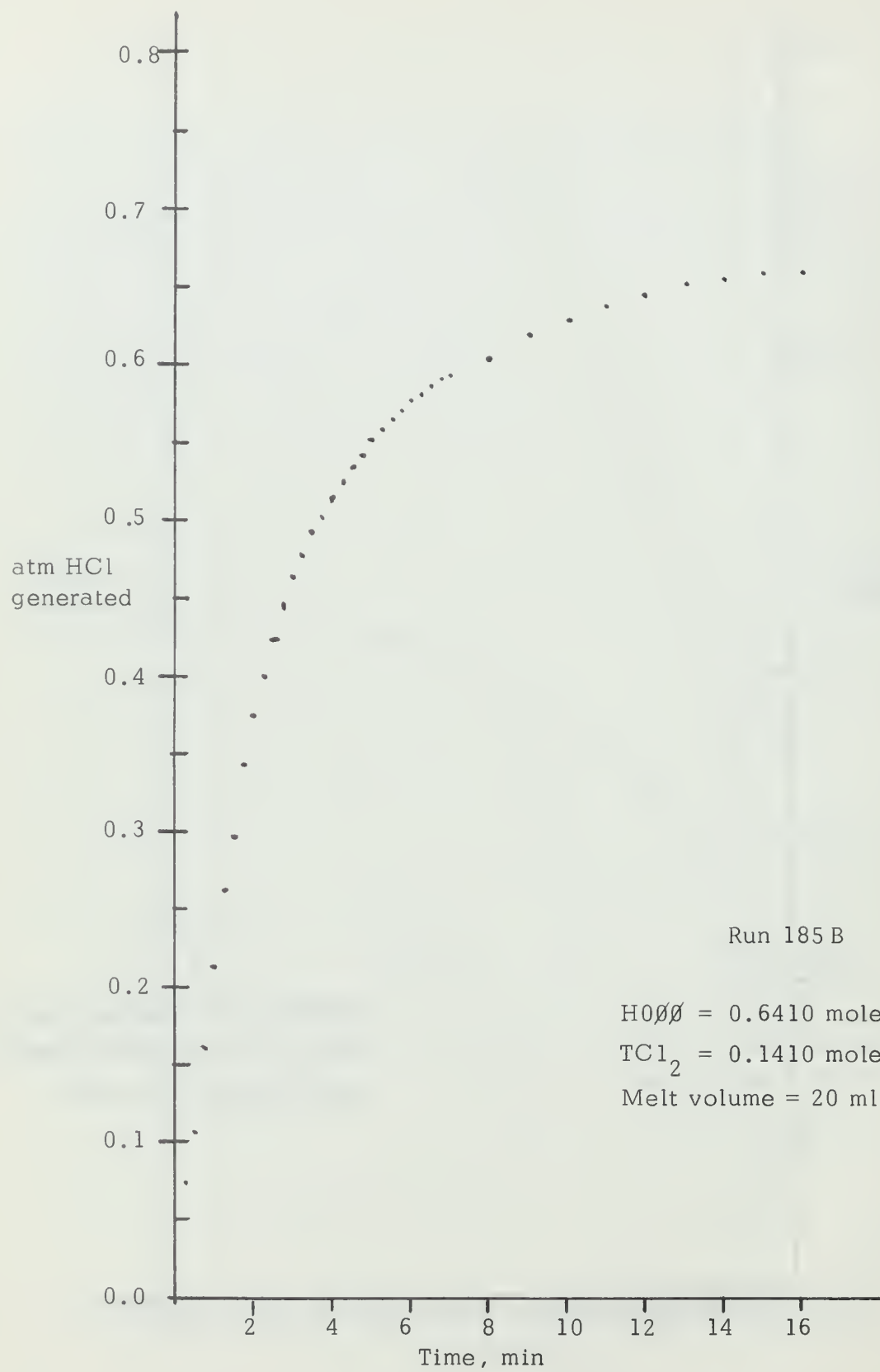
D = intermediate C l T 0∅∅

P = product T(0∅∅)$_2$

A virtual reproduction was obtained for runs 195C and 185B. All the other curves agreed with the plotted data during the first 50% of the reaction and also during the last five minutes of the plotted data. The only variance occurred at the bend in these curves and the deviation never exceeded 0.05 atm. The rate constants have been averaged for the runs and are presented in Table I.

<div align="center">TABLE I</div>

Temp.	k_1	k_2	k_{-1}	k_{-2}	k_{eq}
195	1.82±.15	.784±.1	.633±.1	1.27±.1	1.782
185	1.29±.15	.379±.1	.633±.1	1.27±.1	.638

Degrees in Centigrade, Rates in liters moles^{-1} seconds^{-1}

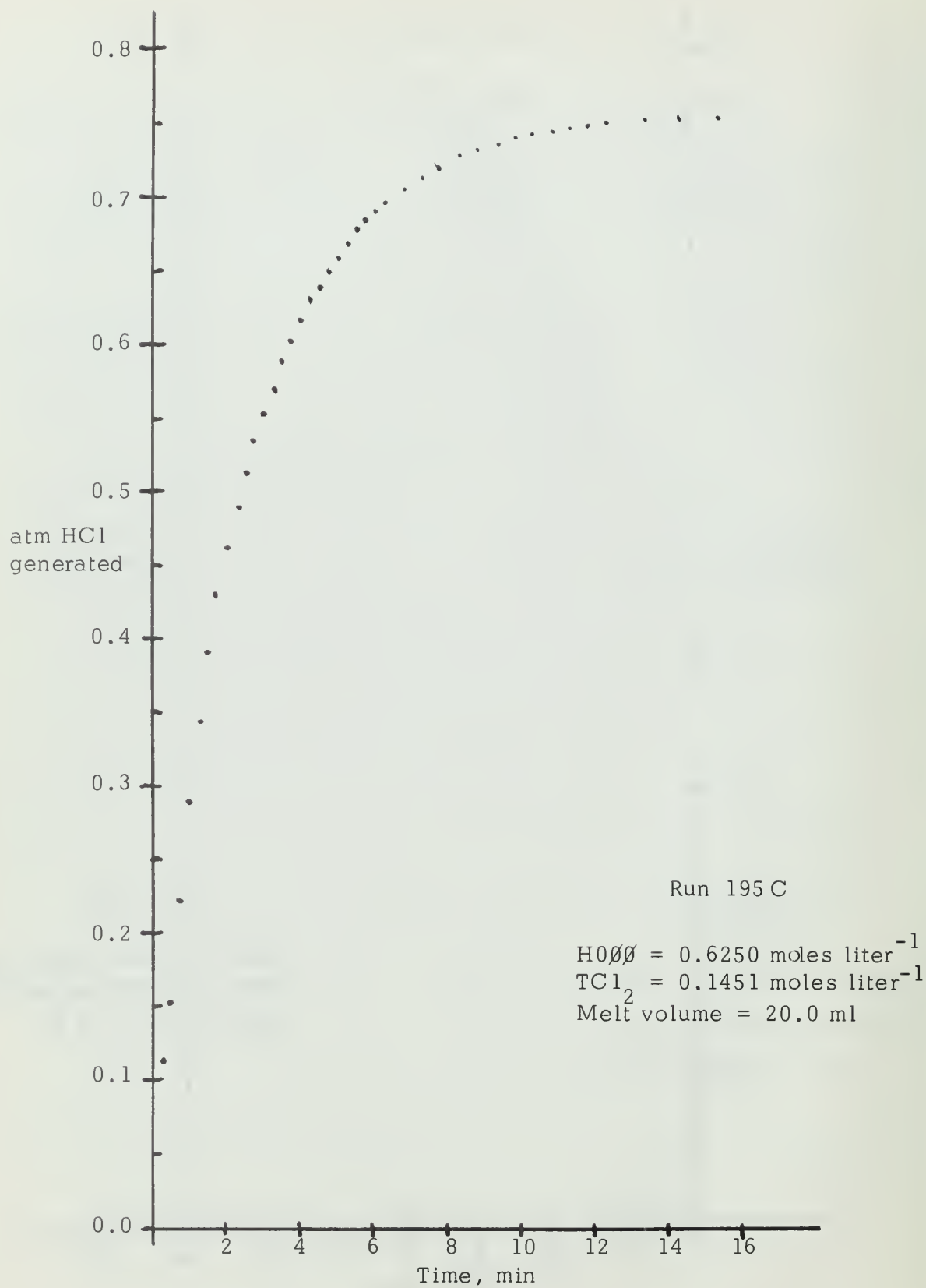In addition, these values were used to extrapolate to a set of rates for 205°C. These values were used in the analog computer with the initial conditions of the run for which the temperature had been raised and lowered through various steps. The output at equilibrium times compared to within 1.5% of the actual pressures observed at equilibrium.

The percentages of HCl titrated and the percent T(0∅∅)$_2$ isolated during the sealed vessel runs are reported in Tables II and III.

The rates of reaction in Table I were used in the thermodynamic relationships,

TABLE II

210° SEALED AMPUOLE RUNS AVERAGE OF TWO RUNS

Time in min.	Percent available HCl determined by titration	Percent $T(0\emptyset\emptyset)_2$ isolated
1.45	0.0	0.0
10.00	28.8	45.0
20.00	31.0	48.0
30.00	30.0	38.0
40.00	23.0	34.0
60.00	15.0	65.0

TABLE III

KOH ABSORBER RUNS AT 210°C

Time in min.	Percent $T(0\emptyset\emptyset)_2$ isolated
4.0	31.1
8.0	62.2
#10.0	60.0
15.5	64.7
20.0	50.1

average value for two runs.

$$\Delta F^{\ddagger} = -RT \ln \left(\frac{k_r h}{KT} \right)$$

$$\Delta H^{\ddagger} = -R \left(\frac{d(\ln k_r)}{d(1/T)} + T \right)$$

$$\Delta S^{\ddagger} = R \left(T \frac{d(\ln k_r)}{dT} + \ln \frac{k_r h}{kT} - 1 \right)$$

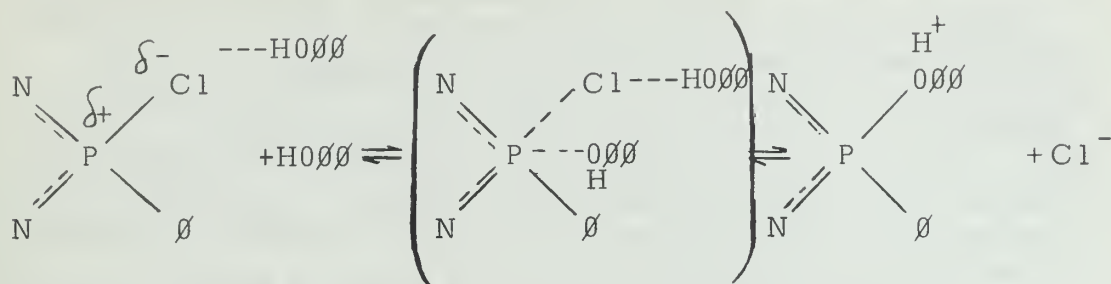to obtain an <u>Entropy of activation</u> of -42.5 ± 10.0 cal mole^{-1} degree K^{-1} and <u>Heat of activation</u> of 13.6 ± 10.0K cal mole^{-1} for the first substitution. The H of the complete reaction is 43.5 ± 10.0 K cal mole^{-1}.

V. DISCUSSION

A. SEALED AMPUOLE DATA

Although the values in Tables II and III are suspect as to how accurately they portray the exact reaction concentrations, certain valuable information was obtained from the closed ampuole runs. First, of course, the fact that commercial analysis shows without a doubt that both chlorides have been replaced, this is significant to the interpretation of the gas pressure studies. Secondly, the data was significant in that it established the order of magnitude of the rate of reaction. Prior to this, based on the long reaction times reported in reference 1, for the reaction involving bisphenol, a slow reaction rate was expected. Third, the isolation of the product in two isomers raises reasonable doubt as to the necessity of purifying the high melting isomer for the polymerization studies. The work reported here does not resolve this question since the purest starting material used in any of the reactions still had a two-degree spread at melting. This spread is not easily interpreted as to the amount of _cis_ TCl_2 this introduces into the reaction at time zero, and might account for the low melting product isolated. There did not appear to be a significant difference between the amount of _cis_ material isolated when comparing once and twice recrystalized starting materials.

Taking a combination of the possibilities suggested above, a reaction mechanism is proposed which incorporates them.

$$
\begin{array}{ccccc}
\overset{\delta-}{\underset{N}{\overset{N}{\diagdown}}}\overset{---HO\emptyset\emptyset}{\underset{P}{\overset{Cl}{\diagup}}}\emptyset
& +HO\emptyset\emptyset \rightleftharpoons
& \left(\; \overset{N}{\underset{N}{\diagdown}}\; P \overset{Cl---HO\emptyset\emptyset}{\underset{\underset{\emptyset}{O\emptyset\emptyset}}{\diagup}} \;\right)
& \rightleftharpoons
& \overset{N}{\underset{N}{\diagdown}}\; P \overset{\overset{H^{+}}{O\emptyset\emptyset}}{\underset{\emptyset}{\diagup}}
& +Cl^{-}
\end{array}
$$

This proposed mechanism is in accordance with the views presented in reference 16 on page 370, that greater aromaticity is obtained from the phosphorous d orbital when polarized by electron with drawing groups, thus the phosphorous is going to be in a more stable configuration when it is positively polarized as shown. The high entropy term is then reasonable, if one considers the obvious steric interference of the transition configuration with the added loss in entropy due to tying up an additional solvent molecule. This configuration would also be expected to reduce to some extent any motion that the tetramer normally undergoes when in solution, such as shifting between a boat and chair configuration, generally attributed to the tetramers. This mechanism further would not require a high enthalpy of activation since delocalization is not lost and the strength of an oxygen to phosphorous bond is approximately equal to the chloride to phosphorous bond.

The second substitution should be similar in nature to the first substitution. The data from the analog computer does not support this. Since the system is quite complex during the second substitution, the values for activation should generally be studied with a more refined

B.   GAS PRESSURE STUDIES

The fact that there is considerable uncertainty in the values reported from these studies is understandable, based on the approximations used in establishing the reaction parameters.   A major approximation which is known to have introduced error was that the volume of melt liquid was the same for each run.   The value chosen of twenty ml is considered accurate only to plus or minus one-half of a milliliter.   In addition, there is the error associated with the p-hydroxybiphenyl which sublimed to the level of the hot oil in each run.   A small error was introduced in the calculations because the volume of 136 ml of the gas system is considered accurate to plus or minus one-half a cubic centimeter.   Another error is the one introduced by the temperature gradient which must exist in the reaction vessel since the oil temperature was 180°C above the ambient temperature of the major portion of the vacuum system.

These variances do not prevent some discussion on the values of activation obtained using the reaction rates obtained on the analog computer.   The Entropy of activation of -42.5 ± 10.0 cal per mole degrees K is high.   However, even the lower value of -32.5 suggests that much steric hindrance must be overcome in the transition state.   It further suggests that additional ordering is taking place, which could be attributed to either solvent ordering or loss of freedom by the tetramer during the transition state.   The relatively low value of Enthalpy of activation of 13.6 ± 10.0 would indicate that if there is any ring delocalization, it is not lost during the transition state.

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system than that used here, and it is not suprising that the data does

not support the view that both reactions should operate through the

same mechanism. But in defense of why the two reactions should

follow the same route, it can be said that the biphenyl oxide should be

just as efficient at polarizing the phosphorous as the chloride, and by

the time any difference is transmitted around the ring to the second

reaction site, it should have no effect on the next reaction.

There still remains the question of the existence of the proposed

intermediate. The failure to isolate it does leave doubt as to its

existence. The most logical place to have found the intermediate

would have been in the material which was treated by sublimation during

the KOH absorber isolation steps. The elemental analysis and the ir

data of the material remaining after the removal of the p-hydroxybiphenyl

show a probable mixture of high and low melting product. The chloride

content suggests the presence of a small amount of either TCl_2 or the

proposed intermediate. If, in fact, there was some TCl_2 or intermediate

present, the sublimation conditions could easily destroy them. That is,

with a temperature of 130°C and a continuous withdrawal of gas, a

potential exists to drive the intermediate and/or TCl_2 to product.

VI. CONCLUSION

The reaction of substituting an alcohol for chloride on the tetramer of phosphonitrile is extremely fast at temperatures in the range of 200°C. The speed at which this reaction takes place at this temperature precludes the formation of long chain polymers due to the fact that too many initiations take place, thereby using up available reaction sites before satisfactory chain lengths have been reached. The only hope for long chain polymerization is in poisoning the reaction melt or by locating a satisfactory solvent for lower temperature work.

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13. ABSTRACT

In this research, a study of the kinetics and mechanism of the biphenyloxide substitution for chloride on the hexaphenyldichlorotetraphosphonitrile molecule was conducted. The reaction was studied in sealed, evacuated ampuoles at 210 °C and in an evacuated gas pressure measuring system at temperatures of 185°C and 195°C.

Two isomers of the expected disubstituted product were isolated by fractional recrystalization from acetonitrile. The isomers had melting points of 204°C and 174°C.

The gas pressure studies provided extent of reaction versus time curves. An analog computer was used to simulate the reaction and the rates obtained were used to determine the Entropy of activation as -42.5 ± 10.0 cal mole^{-1} degree K^{-1} and Enthalpy of activation as 13.6 ± 10.0 Kcal mole^{-1} for the first substitution.

A mechanism consistent with these values is proposed and discussed.

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	ROLE	WT	ROLE	WT	ROLE	WT
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Phosphonitrile						
Inorganic Polymer						